

The Chemical Comparison of Four Cigar Filler Tobaccos. I. Preliminary Investigation of Mainstream And Sidestream Smoke

2788

By S. Osman and J. Barson¹

Eastern Utilization Research and Development Division, ARS,
U. S. Department of Agriculture, Philadelphia, Pa., U.S.A.

Introduction

In the past our research has been concerned with chemically characterizing cigar smoke condensate. In recent publications, for example, we discussed the characterization of a portion of the acid fraction (3) and some neutral components (4, 5). We have now initiated, along with this research, a study to determine chemical differences among four commonly used cigar filler tobaccos and their corresponding smoke. It is our hope that this approach will enable us to determine what chemical constituents of the smoke can be related to smoking quality since the manufacturer apparently blends these tobaccos to obtain a preferred smoking quality. This paper will discuss some preliminary results obtained on the smoke.

Although we had at our disposal semi-quantitative methods that were developed in our general study of the smoke condensate we chose to apply more direct analysis of the total smoke in the initial phase of this investigation. This approach has obvious disadvantages where subtle differences are involved or where there are differences in very minor constituents; however, gross differences, and in some cases even minor differences, can be detected with the minimum amount of manipulation of the smoke giving, we believe, a more accurate picture of the smoke composition (artifacts and losses due to the isolation procedure are avoided). The increased developments in gas chromatography has made such an

approach much more feasible today than ever before (2). In fact, this approach is being expanded as new techniques in gas chromatography become available to us.

Experimental

Analysis of Gas Phase Components of Mainstream Smoke

A sample of mainstream smoke was delivered directly to the gas chromatography by means of a standard gas sampling device. The gas sampler was adjusted to deliver approximately 5 ml of smoke. The particulate matter of the smoke was removed by a Cambridge filter that was inserted between the gas sampler and the cigar. The equivalent of three puffs (35 ml) were taken in succession through a gas sampling valve of 5 ml capacity. The sample was chromatographed on a Varian-Aerograph Model 1520 Gas Chromatograph² after three puffs had been collected in the sampling tube. The column was 50 ft x 1/8 in. stainless steel packed with Chromosorb W (45-60 mesh) coated with FFAP liquid phase (18%). The column temperature was programmed from 55°C to 125°C at 1°C per min. Carrier gas (helium) flow was adjusted for 30 ml/min at 55°C; injector and detector temperatures were maintained at 150°C.

Analysis of Sidestream Smoke

Using standard smoking conditions (7), the smoke emitted from the burning end of the cigar was collected in a 250 ml filter flask. The sidearm of the flask was fitted with an eyedropper bulb and a loose seal was made between the cigar and the flask by means of a cork stopper. After collecting the smoke a 5 ml aliquot was withdrawn from the flask, through the eyedropper bulb on the sidearm, using a gas tight syringe; this sample was rapidly injected into the gas chromatograph. Chromatograph conditions were the same as those described for the analysis of the vapor phase mainstream smoke.

Analysis of High Boiling Compounds in Mainstream Smoke

Eight cigars were smoked under standard conditions (7). The smoke traps were washed with 30 ml of diethyl ether at ambient temperatures; the diethyl ether solution was dried over anhydrous sodium sulfate for 24 hours (at 4°C) then concentrated to 5 ml on a rotating vacuum evaporator at 10°C. An aliquot of the concentrated sample was subjected to gas chromatographic analysis under the following conditions: column, 5 ft x 1/8 in. stainless steel tubing packed with Chromosorb W (60-80 mesh) coated with SE-30 (13%); helium flow rate, 30 ml per min; column temperature programmed from 75°C to 210°C at 2°C/min; detector

¹ Senior and Junior Research Fellows, respectively, Cigar Manufacturers Association of America.

² Mention of a specific commercial product does not constitute an endorsement by the Department over similar items not mentioned.

and injector temperature, 250°C.

Component Characterization

Isoprene was identified by combined gas chromatography and mass spectrometry. The effluent from the column exit port of the gas chromatograph was split so that the major portion went directly into the mass spectrometer (CEC Model 103), and the remainder to a flame ionization detector. Scans of 15 sec duration were taken at different points as the material eluted (total peak elution time was 30-40 sec). The spectra gave very good agreement with that of a standard isoprene sample and very little impurity could be detected.

Nicotine, limonene and neophytadiene were identified by collecting chromatographic eluates by techniques previously described (6) and subjecting these eluates to infrared and mass spectral analysis.

Results and Discussion

Four experimental cigar types were prepared for this study under the supervision of the Cigar Manufacturers Association of America. The cigars were similar in all respects (wrapper, binder, size and shape) except for the filler tobaccos. The individual types contained the following filler tobaccos: Pennsylvania, Puerto Rican, Colombian and Dominican.

The "vapor phase mainstream smoke" was studied initially. Vapor phase smoke, in this case, refers to that portion of the smoke which passes through a Cambridge filter. The cigars were smoked directly into the gas chromatograph with the aid of a gas sampling valve. A typical chromatogram of a 5 ml aliquot from a single 35 ml puff is shown in Figure 1 (using conditions described in Experimental Section). A variety of other chromatographic conditions using available equipment did not significantly increase the resolution of these components although we recognize the fact that the use of capillary columns should show major improvements in this regard. In Table 1 the corresponding peaks in the chromatograms of the four cigar types are compared on an area basis (in correlating these values only relative comparisons within a chromatogram are meaningful since the amount of total smoke that is delivered to the chromatographic column will vary from run to run). For example, the ratio of the area of peak 1 to 2 in the Puerto Rican filler smoke is al-

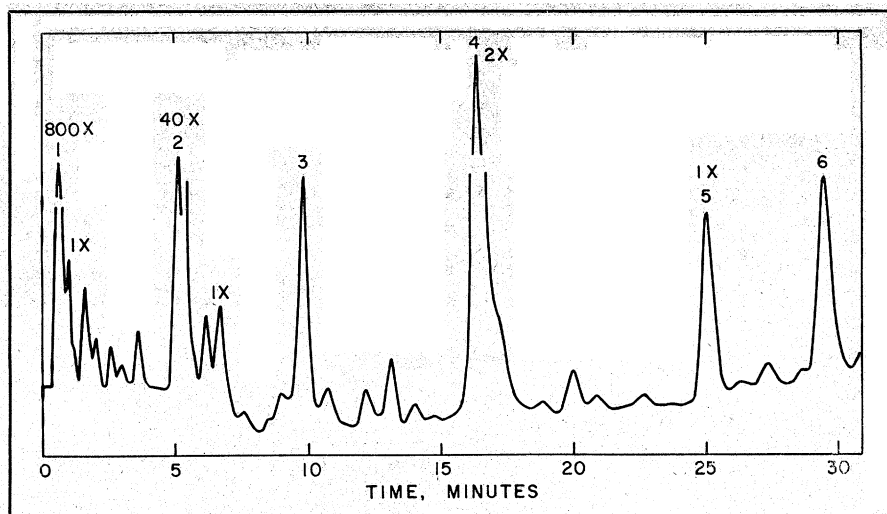


Figure 1. Chromatogram of vapor phase mainstream smoke.

most twice that of the Colombian filler smoke. From the other values it would appear that the reason for this difference between the Puerto Rican and Colombian smoke is the unusually greater area of peak 2 in the Colombian sample. The lower value for the area of peak 1 in Colombian smoke could be a function of the amount of smoke analyzed since all the other Colombian peak areas measured are of an equally lower magnitude than those found for the Puerto Rican smoke. Peak 2 was identified by combined gas chromatography and mass spectrometry as isoprene. The fact that isoprene is more abundant in the Colombian smoke is not too surprising in light of results we will discuss presently. Other differences that appear

in Table 1 are of too small a magnitude to draw meaningful conclusions.

The "vapor phase sidestream smoke" was collected from the burning end of the cigar in a filter flask. An aliquot of the smoke that did not immediately condense on the walls of the flask was chromatographed and showed similar quantitative and qualitative differences (Table 2) as the mainstream smoke. The chromatographic variations that are apparent between the sidestream and mainstream smoke of a particular cigar type may be due to differences in sampling techniques.

A preliminary investigation of the high boiling compounds in the mainstream smoke (i.e. that portion of the mainstream smoke which is not

Table 1. Area comparison of components in the "Vapor Phase" mainstream smoke

Peak no. ^a	Pennsylvania	Puerto Rican	Colombian	Dominican
1	1.4×10^3	1.6×10^3	1.2×10^3	1.4×10^3
2 ^b	384	392	528	352
3	40	35	34	45
4	90	118	80	100
5	25	39	25	37
6	38	40	35	40

^a See Figure 1.
^b Isoprene

Table 2. Area comparison of components in the "Vapor Phase" sidestream smoke

Peak no.	Pennsylvania	Puerto Rican	Colombian	Dominican
1	568	640	400	624
2 ^a	110	86	140	100
3	27	27	26	20
4	7	6	2	6
5	10	10	13	10

^a Isoprene

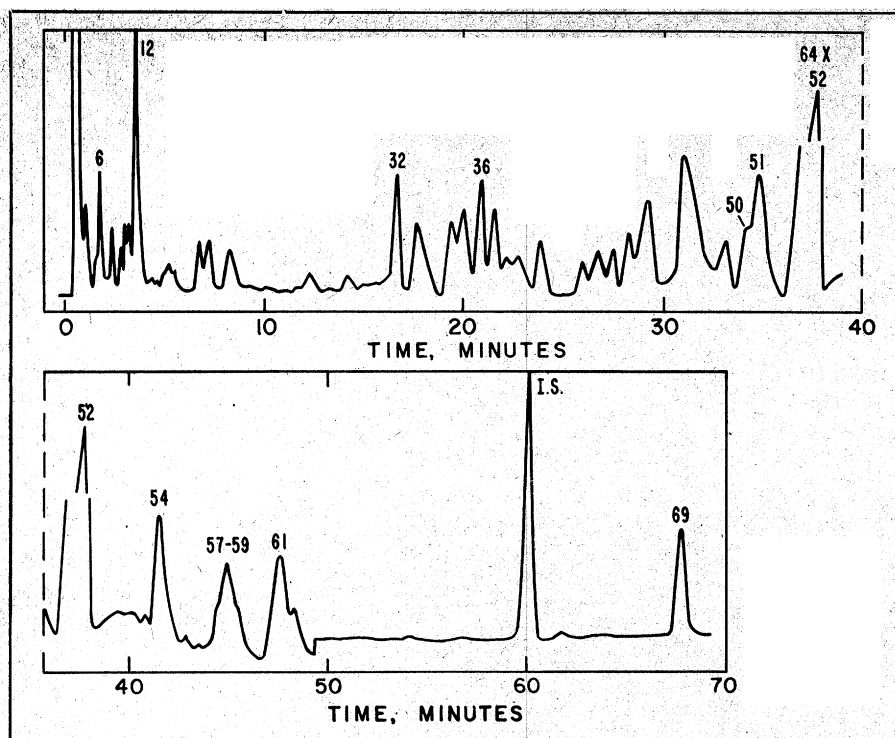


Figure 2. Chromatogram of high boiling compounds in mainstream smoke.

Table 3. Area comparisons^a of components in the "High Boiling" mainstream smoke

Peak ^b	Pennsylvania	Puerto Rican	Colombian	Dominican
32	1.3	1.0	2.8	1.3
52	2.6	1.0	1.6	1.1
54	4.1	1.0	5.7	3.4
61-62	1.7	1.0	2.3	1.5
69	1.8	1.0	3.0	1.5

^a Values represent peak areas relative to corresponding peak in Puerto Rican type.

^b See Figure 2.

eluted under conditions used in investigating the vapor phase) has shown further chemical differences among the four cigar types. The method used to characterize this fraction has several limitations which we are attempting to eliminate; however, definite differences are readily apparent. A typical chromatogram of this fraction is shown in Figure 2. I.S. refers to heptadecane which was used as an internal standard. Relative comparisons were made for the same peak in the four cigar types rather than comparing areas for different peaks within a cigar type. The results in Table 3 indicate that smoke from the Pennsylvania type is high in nicotine (peak 52) and along with the Colombian type high in an un-

identified component (or components) represented by peak 54. The greatest number of differences appear in the smoke of the Colombian tobacco. It contains relatively large amounts of limonene (32) and neophytadiene (69) which is consistent with the fact that we also find large amounts of isoprene in the vapor phase of the Colombian smoke (terpenes are a likely source of isoprene in the smoke, and limonene may also be formed by the dimerization of isoprene (1)). It is interesting that relatively large amounts of phenylacetic acid are found in the Colombian smoke (3). This compound has strong olfactory properties and it is readily detected (by odor) when eluting from the gas chromatograph. In fact, under the chromatographic

conditions described in the Experimental Section, the odor from the phenylacetic acid is the most characteristic one detectable in this fraction (even though phenylacetic acid is a minor component).

The high boiling fraction of the Dominican and Puerto Rican smoke appear to be quite similar; however, the Dominican smoke contains somewhat greater amounts of limonene (32), phenylacetic acid, neophytadiene (69) and peak 54 (unidentified).

In conclusion a few simple chromatographic analyses have uncovered many chemical differences between smoke obtained from four cigar filler types. The relationship of these differences to smoking properties such as flavor and aroma remains to be determined. As we indicated at the beginning of this paper, these results are preliminary. We have only examined quantitative differences for those compounds that chromatograph under the conditions used. Also, many of the peaks observed in the chromatogram may represent more than one component which may obscure differences between cigar types

Acknowledgment

The authors thank the Cigar Manufacturers Association of America for their support of this work.

Literature Cited

1. Grossman, J. D., R. M. Ikeda, E. J. Deszyck and A. Bavley. Mechanism of solanesol breakdown during pyrolysis. *Nature* 199: 661-663. 1963.
2. Hornstein, I. and R. Teranishi. The chemistry of flavor. *Chem. Eng. News* 45 (15): 93-108. 1967.
3. Osman, S. and J. Barson. An aromatic acid fraction of cigar smoke condensate. *Phytochem.* 5: 511-515. 1966.
4. Osman, S., J. Barson and C. J. Dooley. Paraffins of cigar smoke. *J. Assoc. Offic. Agr. Chemists* 48: 1059-1062. 1965.
5. Osman, S. and J. Barson. The isolation of farnesyl acetone from cigar smoke condensate. *Tob. Sci.* 10: 85-87. 1966.
6. Osman, S. and J. Barson. The volatile bases of cigar smoke. *Phytochem.* 3: 587-590. 1964.
7. Schepartz, A. I. The chemistry of cigar smoke. I. An automatic smoking machine for cigars. *Tob. Sci.* 3: 144-147. 1959.